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**EVALUATION OF ORGANIC FLUORINE COMPOUNDS
FOR USE IN MILITARY AIRCRAFT**

HAROLD ROSENBERG

J. C. MOSTELLER

MATERIALS LABORATORY

APRIL 1955

WRIGHT AIR DEVELOPMENT CENTER

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EVALUATION OF ORGANIC FLUORINE COMPOUNDS FOR USE IN MILITARY AIRCRAFT

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**WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

This report covers material presented as a paper before the Fluorine Symposium, Division of Industrial and Engineering Chemistry, at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J.

It was prepared by the Organic Materials Branch under Project No. 7340, "Rubber, Plastics, and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers"; Project No. 7331, "Hydraulic Fluids", Task No. 73313, "Hydraulic Fluids"; and Project No. 3044, "Aviation Lubricants", Task No. 73314, "Lubricants"; formerly RDO No. 613-15, "Hydraulic Fluids and Lubricants"; and was prepared by Dr. Harold Rosenberg and Mr. J. C. Mosteller of the Materials Laboratory, Directorate of Research, Wright Air Development Center.

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ABSTRACT

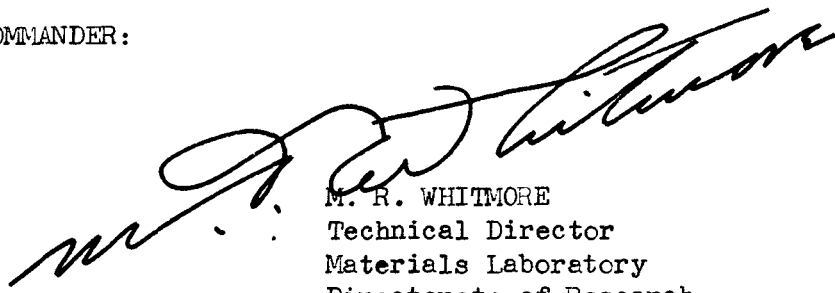
The evaluation of fluorine compounds for use in military aircraft is one phase of a general Air Force program which has been established for the purpose of obtaining materials of unusual properties and capable of advancing the design of new high-speed aircraft and guided missiles. The desirable properties of fluorine-containing organic compounds include wide liquid range, unusual chemical stability, good electrical conduction, desirable heat transfer characteristics and decreased flammability. Fluorine compounds have, accordingly, been studied for use as fire-extinguishing agents, acid-resistant coatings and greases, non-flammable hydraulic fluids, elastomers, electronic equipment and fungicides.

For extinguishing aircraft fires, particularly those involving rocket-propellant mixtures, dibromodifluoromethane and bromotrifluoromethane have been shown to be quite effective. Polymers of monochlorotrifluoroethylene and tetrafluoroethylene have been employed successfully as seals, gaskets and in lubricants in aircraft reaction motors and nitric acid-refueling trailers. Various fluorocarbons, especially chlorofluoroheptenes, have been evaluated as "snuffer" and anti-wear additives for hydraulic fluids. Amongst the "fluoroelastomeric" materials, the poly-1,1-dihydroperfluoroalkyl acrylates have shown the most promise from the standpoint of solvent resistance and low-temperature flexibility. Polyfluoroethylene derivatives have found use in electronic components of military aircraft. Recently, fluorodinitrobenzenes have been shown to be effective agents for protecting fabrics against fungi attack.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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INTRODUCTION

In order to obtain materials possessing unusual properties and capable of withstanding the extremes of temperature and operating conditions encountered in new high-speed aircraft and guided missiles, the U. S. Air Force during recent years has been conducting investigations into various fields of chemistry. One class of substances which has been studied quite extensively and in which work is continuing is that of fluorine-containing compounds. A preliminary evaluation of the work being conducted under this research program was presented in an earlier paper (Ref. 1).

As a result of the investigations on fluorine-containing materials conducted by and for the Air Force during the past several years, many of the desirable properties and advantages of these compounds have been further exploited to permit application in military aircraft. Unfortunately, certain limitations of this class of compounds have been uncovered which prevent, in part, their full utilization by the Air Force. Of the many potential uses considered for fluorine compounds and for which evaluation studies have been carried out, only the more significant applications will be discussed at this time. These include use of fluorine-containing materials as fire-extinguishing agents, acid-resistant coatings and protective materials, non-flammable hydraulic fluids and lubricants, rubber-like materials, components of electronic equipment, and fungicides.

I. FIRE-EXTINGUISHING AGENTS

Following World War II the Air Force employed methyl bromide (and more recently, bromochloromethane) as the fire extinguishing agent in military aircraft. This compound is, in general, more effective than the agents previously used, such as carbon tetrachloride, but was found to possess certain significant limitations. The toxicity and corrosiveness of methyl bromide were sufficiently great to cause the Air Force to seek other materials as effective as the halocarbon but less toxic and corrosive in nature.

As a result of an extended investigation conducted by Purdue Research Foundation under the sponsorship of the Army Engineers Research and Development Laboratories and, later, under the Air Force, a number of fluorocarbons were shown to be more effective than methyl bromide as a fire-extinguishing agent (Ref. 2). Of this group, several

TABLE I

COMPARISON OF FLUORINE-CONTAINING AND
NON-FLUORINE-CONTAINING EXTINGUISHING AGENTS

<u>Formula</u>	<u>Agent Name</u>	<u>Mol. Wt.</u>	<u>B.P., °C</u>	<u>Peak in Order of Effectiveness</u>		<u>Toxicity PPM.^b</u>
				<u>Flamm. Curve, %</u>	<u>Volume Basis</u>	
CBrF_2	Dibromodifluoromethane	209.8	24.5	4.2	1	55,000
$\text{CF}_2\text{BrCF}_2\text{Br}$	Dibromotetrafluoroethane	259.9	46.4	4.9	2	126,000
CF_3Br	Bromotrifluoromethane	148.9	-57.8	6.1	3	800,000
CH_2BrCl	Bromochloromethane	129.4	68-69	7.6	4	64,000
CH_3Br	Methyl bromide	95.0	4.5	9.7	5	6,000

^a Per cent of extinguisher required to reduce the flammability of mixtures of air and n-heptane.

^b Average lethal concentration for rats on 15 min. exposure. Data obtained from toxicity studies carried out by the Army Chemical Center (Ref. 3).

compounds, presented with certain of their properties in Table I in comparison to other common extinguishers showed exceptional promise. These were evaluated further as extinguishing agents for rocket fuel fires in a second study conducted by Purdue under contract to the Air Force (Ref. 4). In this investigation, 1,2-dibromotetrafluoroethane was found to be, in general, the most effective extinguisher while dibromodifluoromethane ranked second. The latter compound, shown to be the most effective of all compounds tested in the earlier Purdue studies, was recently found, together with bromotrifluoromethane, to be highly successful in extinguishing full-scale rocket-propellant fires (Ref. 5). The Aerojet Engineering Corporation, in work performed under Air Force sponsorship, has demonstrated that it is feasible by use of either of these two materials, to protect piloted rocket-powered aircraft from fire and explosion hazards involving such propellant combinations as WFNA (white fuming nitric acid) and JP-3 (formula assumed as C_6H_6) fuel. The two fluorocarbons, as can be seen from the data presented in Table II, are completely effective in extinguishing fires. Although bromotrifluoromethane appears to be slightly more efficient in terms of amount of agent required, dibromodifluoromethane is believed to be the more practical agent for use in rocket aircraft because of its high density, relatively high boiling point, and relatively low vapor pressure at elevated temperatures.

II. ACID-RESISTANT COATINGS AND PROTECTIVE MATERIALS

Fluorine-containing materials are being used with much success in sealing and gasketing materials in aircraft reaction motors. They are also now employed as lubricants as well as for gaskets and seals in nitric acid-refueling trailers. Polymers of monochlorotrifluoroethylene and tetrafluoroethylene, such as Kel-F and Teflon, are utilized as flanged dynamic seals and as static gaskets in the oxidizer, fuel and air systems of the reaction motor. The lubricants used in these motors are primarily fluorocarbon oils and grease-like materials, such as Fluorothene G and O or Fluorolube derivatives, all being polymers of fluorinated ethylenes. The fluorocarbon oils are used where lubrication is required for moving parts in contact with nitric acid-type oxidizers over the temperature range of -65 to 160°F . The heavier grease-like substances, such as Fluorothene G, are used particularly for sealant purposes where it is desirable to prevent entry of oxidizer fumes or necessary to protect materials lacking somewhat in corrosion resistance to such fumes.

The nitric acid-servicing trailers employ the same fluorocarbon oils and grease-like materials that are used in the rocket motors. However, greases which are used to lubricate the pump bearings in these

TABLE II

RESULTS OF WFNA-JP-3 SPRAY FIRE-EXTINGUISHMENT
TESTS WITH VARIOUS EXTINGUISHING AGENTS^a

Formula	Agent Name	Agent Discharge Rate, lbs./sec.	Total Agent, lbs.	Result
CH ₃ Br	Methyl bromide	9.0	9.0	Fire not affected by agent
CH ₂ BrCl	Bromochloromethane	10.6	5.52	Fire not affected by agent
CF ₂ Br ₂	Dibromodifluoromethane	5.7	1.5	Fire extinguished immediately
CF ₃ Br	Bromotrifluoromethane	5.5	0.7	Fire extinguished immediately

^a Conducted with "fire size", or propellant flow rate, of approximately 0.2 lb./sec.

trailers are required to be resistant not only to the concentrated oxidizers but also to various aqueous mixtures as well as to water itself. The fluorocarbon greases have thus far been deficient as lubricants due to their poor stability in remaining as grease-like materials under applied load and to their lack of water resistance which results in rusting of the pump bearings.

External portions of rocket motors or of the aircraft housing the rocket assembly are primarily constructed of materials inherently resistant to corrosion, such as corrosion-resistant steel or aluminum alloys. Paints and chemical coatings for corrosion protection have not been applied very successfully to rockets using nitric acid-type oxidizers. Teflon and Kel-F paints have been used experimentally but their applicability appears to be quite marginal. Such coatings are not impervious to nitric acid attack and, in addition, require that the part coated be subjected to temperatures of 450°F and higher in order for the paint to "set". Some non-fluorine-containing paints which resist nitric acid fumes, such as vinylite or chlorinated rubber-base paints, are fairly satisfactory except that they are readily soluble in the rocket fuel used in combination with the oxidizer. Thus, spilling of the fuel often results in dissolution of the paints and lack of nitric acid protection to metal surfaces.

III. NON-FLAMMABLE HYDRAULIC FLUIDS AND LUBRICANTS

In the development of hydraulic fluids for military aircraft, certain properties or characteristics are desired of the fluids. These may be classified in the following manner:

- A. Non-flammability
- B. High viscosity index
- C. Wide liquid range
- D. Stability
 - 1. Thermal
 - 2. Hydrolytic
 - 3. Low-temperature
 - 4. Oxidation-corrosion
- E. Lubricity

Some of the disadvantages of the hydrocarbon-base hydraulic fluid currently used by the Air Force are inflammability and oxidative instability at elevated temperatures. Diester base lubricants, using di-2-ethylhexyl sebacate as the base stock oil, have now been developed by

the Air Force which permit utilization at temperatures above 400°F. However, these blends which are already employed in certain applications, are inflammable and would be hazardous if used as hydraulic fluids in military aircraft. To overcome these limitations, the Air Force has been conducting a research and development program directed along two main paths.

The first approach involves the development of non-flammable materials for addition as "snuffer" additives to flammable base stocks to produce less flammable fluids. The other course is concerned with the synthesis of non-flammable base stock oils for use with other additives to obtain desired blends. Fluorine-containing materials have been considered and studied in both of these connections because of their well-known properties of decreased flammability, exceptional stability, inertness to chemical attack and excellent lubricity.

Amongst the most promising substances examined as "snuffer" additives are tetrachlorodecafluoroheptane, chlorofluoroheptenes, and low molecular-weight polymers of monochlorotrifluoroethylene. These materials were found to be quite effective in "snuffing" such flammable base stocks as mineral (hydrocarbon) oils, silicates and diesters. However, difficulty has been encountered in preparing blends of these additives and base stock oils so as to obtain fluids having desirable viscosity-temperature characteristics, low-temperature stability and decreased volatility. On the other hand, it was noted quite early that certain of these polyhalo compounds possessed excellent lubricity and could be used to improve the wear characteristics of hydrocarbon base oils. It has since been shown that the anti-wear properties of the polychlorofluoro materials can also be extended to other base stocks, such as the silicones which, by themselves, exhibit poor lubrication characteristics. This was found to be particularly true in the case of such compounds as the chlorofluoroheptenes, which are quite effective anti-wear additives for silicones as can be seen from the data in Table III. There is also some evidence that these fluorinated alkenes may, in addition, prove of value as extreme-pressure additives. Lately, a ternary blend of a silicone, fluorocarbon, and diester was prepared which shows promise as a hydraulic fluid not only from the standpoint of lubricity, but also from that of decreased flammability.

Recently, the Air Force has undertaken the investigation of another class of fluorinated materials, namely, the fluorine-containing diesters, as another source of hydraulic fluid oils or additives. A number of these compounds have been prepared in the Air Force laboratories and are now undergoing evaluation studies. Preliminary evidence indicates that certain of these materials may be less flammable than their hydrocarbon analogs while still retaining many of the desirable lubricant properties of the non-fluorinated diesters.

In the consideration of materials for use as non-flammable base stock oils various halogenated compounds, such as hexachlorobutadiene and polymers of monochlorotrifluoroethylene, have been investigated. While these substances are non-flammable they possess certain undesirable properties. The butadiene derivative is exceedingly toxic while the fluorinated compounds exhibit very poor low-temperature characteristics. While other materials such as brominated benzenes (Ref.6), polyglycols and phosphate esters show some promise, no completely acceptable non-flammable base oil has been prepared to date.

TABLE III

EFFECT OF A CHLOROFLUOROHEPTENE UPON THE WEAR
PROPERTIES OF A SILICONE AS SHOWN BY SHELL-4-BALL TESTS

Composition of Fluid, Parts by Weight		Average Wear Scar Diameter (mm.), Steel on Steel Bearing Surfaces	
<u>Silicone</u>	<u>Chlorofluoro- heptene</u>	<u>4.0 Kg. Load</u>	<u>40.0 Kg. Load</u>
10	0	0.376	2.415
9	1	0.244	0.758
8	2	0.252	0.854
7	3	0.300	1.006
6	4	0.346	1.085
0	10	0.318	1.102

IV. RUBBER-LIKE MATERIALS

It is well known that major improvements must be realized in certain properties of elastomeric materials if they are to keep pace with advances in aircraft and missile designs. New fuels, coolants, lubricants and hydraulic fluids, combined with requirements for operation at both higher and lower temperatures than necessary heretofore, pose problems which cannot be satisfactorily resolved by selective copolymerization of conventional monomers, nor by the judicious compounding of presently available synthetic rubbers.

Since every known elastomer has its own peculiar virtues and shortcomings, compromises are accepted of necessity in compounds for many applications even though such compromises may be of a most undesirable nature. Serviceability at -65°F , for example, is obtained in a Buna N rubber by the use of plasticizers but at the expense of poorer ozone resistance as well as decreased tensile strength, set, abrasion resistance and other mechanical properties. If contact with organic solvents is also involved in the application (as it usually is where Buna N Compounds are concerned) the plasticizer will inevitably be leached out and low-temperature flexibility lost. However, the rubber item may continue to function satisfactorily at low temperatures as long as it is swollen by the medium, i.e., to the extent that the organic solvent can penetrate the rubber and act as a plasticizer. Applications which require resistance to excessive swelling by various synthetic oils and hydraulic fluids at elevated temperatures (e.g. above 400°F) present even more difficult problems.

In recognition of the ever increasing urgency of requirements for greatly improved elastomers in a variety of applications, the Air Force has for some time maintained an extensive program of exploratory research directed towards the development of so called "super" elastomers. The major portion of this effort has been in the field of fluorine-containing polymers for reasons which are implicit from study of the structure and properties of commercial plastics of polymonochlorotetrafluoro- and polytetrafluoroethylene. The development of an elastomer which would combine good mechanical properties with some of the thermal stability and chemical inertness of these materials would solve many pressing problems of the Air Force in the rubber field. It has been learned, however, that it is far easier to postulate than to realize experimentally such a fluoroelastomer (fluorine-containing polymer with rubber-like properties).

Several classes of fluorine-containing polymers prepared for the Air Force by Minnesota Mining and Manufacturing Company under this broad

program are of considerable interest in this connection. (Ref. 7) Possibly the most promising class of new fluorine-containing polymers is represented by poly-1,1-dihydroperfluorobutylacrylate, $[-CH_2CH(COOCH_2CF_2CF_2CF_3)-]_n$. This particular polymer is under intense study at the present time as a possible fuel and oil-resistant elastomer. It is almost completely indifferent, as a homopolymer, to the normal swelling action of both aliphatic and aromatic-type fuels and to various synthetic oils of interest in specialized applications. Table IV illustrates the order of solvent resistance and low-temperature flexibility offered by important members of this fluoroalkyl acrylate class as compared with Buna N synthetic rubbers. It will also be noted that the butadiene copolymers of fluoroacrylates are much less sensitive to aromatics than are the corresponding Buna N compounds. Such properties encourage the further investigation and development of these and other fluoroelastomers despite the unique difficulties which have been encountered in connection with the curing and reinforcing of highly fluorinated polymers of a saturated nature. There has been some indication that the polyperfluoroalkyl acrylates have potentialities as fuel and oil-resistant elastomers for high-temperature applications somewhat beyond the capabilities of the Buna N rubbers; preliminary investigation of certain other fluoropolymers also offers encouragement in this respect.

Homopolymers and/or selected heteropolymers have also been prepared from representative members of a number of classes of new or relatively new monomeric materials. In Table V is presented a list of the major classes of monomers which have been screened to date in the continuing quest for fuel and oil-resistant elastomers that will be serviceable far beyond the limitations of the presently known rubbers. In general, the considerations which served as original justification for this work have been confirmed, although it appears that satisfactory low-temperature properties will ultimately be obtained despite, rather than because of, the presence of fluorine in the molecule, especially when the fluorine atoms are located on the "backbone" of the polymer. No extensive attempts have yet been made to extend low-temperature flexibility of these new experimental elastomers by the use of plasticizers. However, it is believed that fluorocarbon plasticizers can be developed which will be compatible with "fluoroelastomers" yet will resist extraction by hydrocarbon solvents. It would be still more desirable, of course, to synthesize an elastomer which would be plasticized internally by virtue of its chemical composition and molecular architecture.

TABLE IV

COMPARATIVE PROPERTIES OF EXPERIMENTAL ELASTOMERS^a

<u>Polymer</u>	<u>Mole % FBA^b, FHA^c, AN^c</u>	<u>T_b^d (°C)</u>	<u>T₁₀^e (°C)</u>	<u>% Swell of Vulcanizate</u>	
				<u>Benzene</u>	<u>70:30 Isooctane/Toluene</u>
Poly-FBA	100 FBA	-15	-6.5	12	0-10
Bu ^f /FBA	11 FBA	-71	-59.0	310	310
Bu/FBA	28 FBA	-62	-41.0	250	150
Bu/FBA	43 FBA	-46	-320.0	70	71
Bu/FBA	82 FBA	-5	-12.0	5	1
Poly-FHA	100 FHA	-39	-6.5	10-20	0
Bu/FHA	24 FHA	-75	-4.2	-	120
Bu/FHA	45 FHA	-43	-36.0	-	72
Polybutadiene	0 AN	< -72	-72.0	930	530
Bu/AN	12 AN	< -72	-42.0	520	230
Bu/AN	23 AN	-60	-31.0	510	95
Bu/AN	43 AN	-27	-7.0	195	35

^a Data compiled under Air Force Contract by Minnesota Mining and Manufacturing Company^b Symbol for 1,1-dihydroperfluorobutyl acrylate^c Symbol for Gehman temperature^d Symbol for acrylonitrile^e Symbol for butadiene^f Symbol for ASIM Brittle Temperature^g Symbol for 1,1-dihydroperfluorohexyl acrylate

TABLE V

SOME CLASSES OF FLUORINE-SUBSTITUTED MONOMERS INVESTIGATED
AS POSSIBLE SOURCE MATERIALS FOR SPECIALTY SYNTHETIC RUBBERS (Ref. 7)

<u>Fluorinated Olefins</u>	<u>Fluorinated Olefinic Esters</u>
Perfluoroolefins	Dihydroperfluoroalkyl acrylates
Fluorinated dienes	Dihydroperfluoroalkyl crotonates
Perfluoronitriles	Dihydroperfluoroalkyl fumarates
Perfluoroalkyl-substituted olefins	Dihydroperfluoroalkoxy acrylates
Perfluoroalkyl-substituted dienes	Vinyl esters of perfluoro acids
Perfluoroalkyl-substituted acrylonitriles	Allyl esters of perfluoro acids

V. ELECTRONIC EQUIPMENT

In the field of electronic equipment, including items such as insulation materials, motor and transformer leads, coaxial cable, high-voltage cable, magnet wire, thermocouple wire and ignition wire, the requirement for materials exhibiting thermal stability, good heat transfer characteristics and low dielectric properties has led to the investigation of fluorine compounds. The properties of some fluorine-containing materials thus far examined explain the reason for the interest in fluorine compounds for such applications. This may be seen from the data in Table VI where voltage breakdown strengths of several fluorinated compounds are compared with those of a hydrocarbon and a halocarbon. Other gaseous, liquid and solid fluorine-containing compounds are of interest for electronic applications and many such materials, particularly of the polyfluoroethylene type, are being employed in our present-day aircraft.

Although fluorine compounds are being utilized with much success in aircraft today, materials with still better properties are desired. Many of these requirements stem from the fact that suitable cooling systems are essential in miniaturized design as the result of efforts to reduce weight and space aboard aircraft. Thus, it is necessary that dielectrics serve a dual purpose, namely that of coolant as well as dielectric. The conventional cooling systems incorporating fans and

TABLE VI

VOLTAGE BREAKDOWN STRENGTHS OF SOME
FLUORINATED AND NON-FLUORINATED DIELECTRICS AT 25°C

Dielectric Material		D. C. Breakdown in KV with <u>0.025" gap (approx. 0.5" diam. spheres)</u>
<u>Formula</u>	<u>Name</u>	
$(C_2F_5)_3N$	Perfluorotriethyl amine	24
$(C_4F_9)_2O$	Perfluorodibutyl ether	27.5
$(C_4F_7)_3N$	Perfluorotripropyl amine	29
$C_8F_{16}O$	Perfluorocyclooctyl ether	29
$(C_6H_{11})_2O$	Perfluorodihexyl ether	30.5
$(C_4F_9)_3N$	Perfluorotributyl Amine	32
CCl_4	Carbon Tetrachloride	18
-	Hydrocarbon Oil (aliphatic-aromatic)	18

blowers impose additional weight which nullifies the advantages of miniaturization. Therefore, means to circulate a low electrical-loss, stable, high-temperature liquid in such equipment are being sought. The fluorine compounds tested thus far are limited by their boiling point. In addition only materials of extreme high purity are desired for dielectrics. As can be seen from Table VII in which data on the dissipation factor of a fluorinated dielectric are presented, purity of product is exceedingly important in this type of applicational use.

An interesting fact noted in connection with most fluorine compounds employed as dielectrics is that they undergo voltage breakdown but recover and do not prevent the continual build-up of energy. In this connection it should be mentioned that certain gaseous fluorinated compounds are being used as dielectrics, Freon and sulfur hexafluoride being the predominant members of this group. However, sulfur hexafluoride, although an excellent dielectric, gives rise under voltage breakdown to decomposition products which are toxic and corrosive.

TABLE VII

EFFECT OF "PURITY" ON DISSIPATION FACTOR
OF PERFLUORODIHEXYL ETHER AT MICROWAVE FREQUENCIES

Purification Stage	Frequency at 25°C			
	<u>10 MCS.</u>	<u>1,000 MCS</u>	<u>3,000 MCS</u>	<u>8,500 MCS.</u>
After 1st Distillation	0.0005	-	0.016	-
After 2nd Distillation	0.0005	0.0037	0.0045	0.004
After 2nd Distillation and silica gel treatment	0.0005	0.0023	0.0028	0.0029

Some solid fluorocarbons are being used to a great extent as coatings for electrical wire and as insulators. Bonding to metallic surfaces, extrusion processes and coatings free from pin holes have been improved to a great extent over the past several years by use of this type of material. One disadvantage, however, is still apparent and may be characteristic of fluorocarbons, namely, that the materials break down due to bombardment of electrons.

VI. FUNGICIDES

Deterioration, weakening and destruction by rotting of cloth and other woven fabrics, thread cordage, leathers and plastics as a result of the growth of molds, or fungi, constitute important factors in the storage, and in use before and after storage, of such materials. Prevention of such deterioration and destruction depends upon protection of fabrics from invasion by fungi. One method of providing protection is by treatment of these materials with fungicidal or fungistatic chemicals.

For this purpose no ideal or perfect chemical has as yet been discovered. Some compounds supply only partial protection while others disintegrate quickly or cause weakening of the fabric. Other fungicides, such as copper-8-quinolinolate, a compound extensively employed by the Air Force, impart undesirable colors, corrode attached metal articles, or prove toxic in contact with human skin. Hence, it is highly desirable that there be available a number of materials with different characteristics, from which may be chosen one adapted to known or anticipated conditions.

One class of materials recently investigated for fungicidal properties and which now shows excellent promise for use as fungicides is that of the fluorobenzenes. A number of such compounds, including fluorinated phenols, quinones, anilines, and nitrobenzenes have been prepared and evaluated for the Air Force by the Illinois State Natural History and Geological Surveys. Of the various groups of compounds tested, the dinitrobenzenes proved most effective as fungistatic agents (Ref. 8). This effectiveness is shown quite markedly in Table VIII where breaking strengths of threads exposed and unexposed to fungi attack were treated with the fluorinated dinitrobenzenes and with copper-8-quinolinolate.

TABLE VIII

BREAKING STRENGTHS OF COTTON PARACHUTE WEBBING THREAD
TREATED WITH FUNGICIDES AND EXPOSED TO MYROTHECIUM VERRUCARIA

<u>Formula</u>	<u>Fungicide Name</u>	<u>Concen-</u>	<u>% of</u>	<u>Pull in lbs.</u>	
		<u>tration, Fungicide</u>	<u>in thread</u>	<u>thread</u>	<u>thread</u>
		<u>mg./liter</u>		<u>exposed</u>	<u>unexposed</u>
$C_6H_2(NO_2)_2F_2$	1,3-Difluoro-4,6-dinitrobenzene	1500	0.31	31.03	30.95
		1000	0.15	23.48	30.76
$C_6H_3(NO_2)_2F$	1-Fluoro-2,4-dinitrobenzene	1500	0.17	31.59	30.75
		1000	0.11	18.16	30.70
$C_6H_2(NO_2)_2FCl$	1-Fluoro-3-chloro-4,6-dinitrobenzene	2000	0.22	28.85	28.86
		1000	0.16	25.48	28.67
$C_6H_2(NO_2)_2FBr$	1-Fluoro-3-bromo-4,6-dinitrobenzene	1000	0.129	31.58	28.61
		750	0.129	31.17	28.93
$C_{18}H_{12}N_2Cu$	Copper-8-quinolinolate	-	1.05	30.8	30.6
		-	1.00	29.6	30.4

The advantage of the fluorobenzenes over the fungicides currently employed for protection of Air Force fabrics is quite significant. They include greater solubility in organic solvents, relatively low concentration

in fabric required to give protection, greater ease of application to fabric and nonrestrictive coloring properties. They also do not promote the oxidation of the materials in which they are impregnated such as in the case with some of the fungicides now in use. The fluorobenzenes, however, are relatively similar in toxicity and corrosiveness to the other fungicides in use, but these disadvantages are far outweighed by their beneficial properties and can perhaps be circumvented in the future.

VII. CONCLUSIONS

From the aforementioned facts and data it can be seen that definite progress has been made in the application of fluorine-containing organic compounds for use in military aircraft. Fluorocarbons, polyfluorocarbons, fluorobenzenes and other fluorine-containing materials are already being employed or will shortly find use as fire-extinguishing agents, acid-resistant coatings and greases, components of electronic equipment and fungicides. However, much work remains for workers in the field of fluorine chemistry before fuller utilization of fluorine compounds can be made in military aircraft. Particularly is this true in connection with the development of non-flammable hydraulic fluids and rubber-like materials. Liquids having wider liquid ranges, improved viscosity-temperature characteristics, and lower vapor pressures are desired. Rubber-like materials with more satisfactory properties of cold flow, resilience, permanent set and hardness, and high-temperature stability must be prepared. However, with regard to the latter, it is certainly safe to predict that aircraft and guided missiles will, in future years, utilize fluoroelastomers as well as the other fluorinated materials described in a number of applications of critical operational importance.

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